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The Cleaning of OAB Universal Covers – An Origin of Smut in Aluminum Alloys

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THE CLEANING OF OAB UNIVERSAL COVERS – AN ORIGIN OF SMUT IN ALUMINUM ALLOYS

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ABSTRACT

The smut that appeared on the universal covers after the OAB cleaning process consists of sub-micron size aluminum particles originating from the machining of these parts prior to cleaning. The rigorous gross and precision cleanings with Brulin in the OAB cleaning process could not completely wash these fine particles away from the surfaces. However, applying a phosphoric acid etch before the cleaning helped to remove these fine aluminum particles. Experimental results again showed that an acid etching before cleaning is essential in preventing the occurrence of smut in aluminum alloy after gross/precision cleaning.

A mechanism, based on the electrostatic ζ-potential, is proposed to explain the occurrence of smut that is often encountered during the cleaning of aluminum alloys.

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INTRODUCTION

In July 2001, the universal covers, made of aluminum alloy 6061-T6 (AA6061) developed "smut" after processing through the Optical Assemble Building (OAB). A detailed description of the OAB gross/precision cleaning process is illustrated in **Appendix I**. Previous experiences on the cleaning of cast aluminum alloy A356 and wrought AA6061-T6 indicated that the smut was generated by the alloy itself during the acid etching [1]. However, the universal covers did not receive any acid or caustic etch prior to the OAB cleaning process. This implies that the smut must come from a different origin.

To trace the origin of the smut, an experiment was conducted to monitor the smut formation at each step of the OAB cleaning process. The OAB cleaning reduced the particles swipe value to level below 83 as shown in **Table I**, however, the smut was still quite visible from the swipe papers as shown in **Figure 1**. This suggests that the size of the particle in the "smut" was much smaller than the 5 μm detecting limit of the Particle Counting Verification System (PCVS). Furthermore, the smut problem seems to be getting worse 24 hours after the precision cleaning as shown in **Figure 1** by the darkening of the smudge on the swipe paper. As a remedial precedure, a phosphoric acid etching process developed previously for NIF[2] was subsequently applied to these universal covers. After the OAB cleaning, the phosphoric acid etched universal covers showed some improvement in the particle swipes values as shown in **Table I**. More importantly, the smut was no longer visible on the swipe papers.

Table I Particle swipe results on un-etched versus phosphoric acid etched universal covers.

	Un-etched Universal Covers		Phosphoric Acid Etched Universal Covers	
	S/N 291	S/N 292	S/N 031	S/N 290
Before Gross Cleaning	193	219	125	90
After Gross Cleaning	-	69	76	54
After Precision Cleaning	66	78	67	79
24-hour after Precision Cleaning	69	70	62	62

This investigation was initiated to 1) determine the origin of the smut in the universal covers or aluminum alloys in general, and 2) answer the perennial question of whether it is necessary to etch the NIF parts made from aluminum alloys before the gross/precision cleaning.

THE NATURE OF THE SMUT

Figure 2 shows the SEM-BSE image of the particles on the swipe paper collected from an un-etched universal cover (S/N292) after the gross cleaning in the OAB. Most of the particles are much smaller than 5 μm. The EDXS analyses were conducted on particles collected from the un-etched universal cover (S/N292) after each step of the OAB cleaning process. **Appendix II** shows the result of the EDXS analyses and the summary of these results is as follows:

Processing Step	Types of Particle found on Swipe Paper
Before Gross Cleaning	Al
After Gross Cleaning	Al, iron oxide and stainless steel
After Precision Cleaning	Al, α-eutectic, iron oxide and stainless steel
24-hours after Cleaning	Al, α-eutectic, iron oxide and stainless steel

The size of the particles in the smut was significantly reduced after each of the cleaning steps, and the majority of the particles were aluminum. After the gross and precision cleanings, some small iron oxide and stainless steel particles from the cleaning tanks were also deposited on the surfaces of un-etched aluminum parts. This suggests that the surfaces of the AA6061 in some way attracted the fine metallic particles during the cleaning process.

THE ORIGIN OF THE SMUT

The experimental results have shown that the phosphoric acid etch effectively removed the smut from the surfaces of the universal cover. Since no universal cover could be sampled for topographical examination on the smut formation, a set of 6061-T6 samples from a previous experiment[2] were selected for SEM study. This set of samples contains four different combinations of surface condition and cleaning steps as illustrated below:

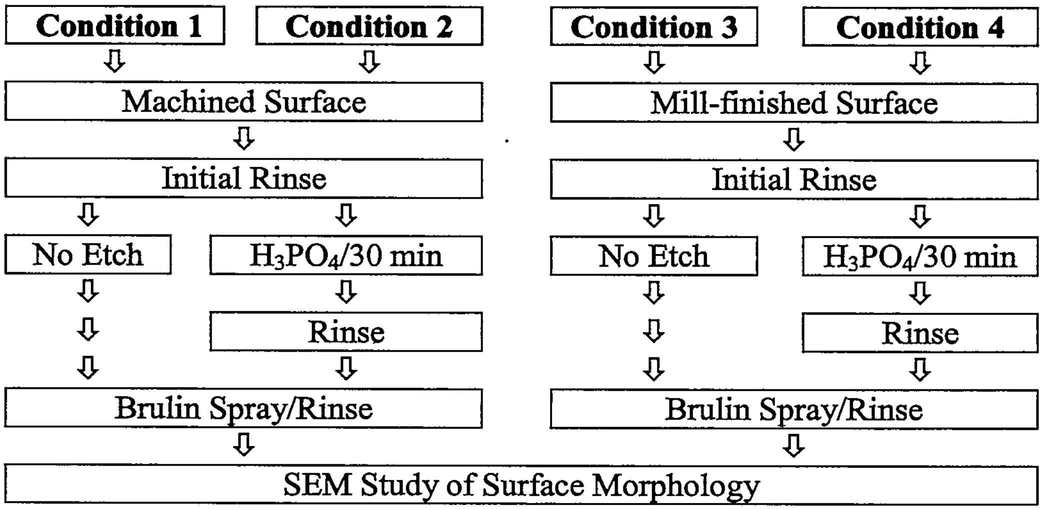

Table II below lists the particles swipe results[2] as affected by the different initial surface conditions and cleaning/ etching steps.

Table II Results of the particle swipe* on AA6061-T6 with machined and mill-finished surfaces.

	Machined Surface					**Mill-finished Surface**				
	Initial Wash	Brulin/ Rinse	Acid Clean	Brulin/ Rinse	After 14 days	Initial Wash	Brulin/ Rinse	Acid Clean	Brulin/ Rinse	After 14 days
	Step I	**Step II**	**Step III**	**Step IV**	**Step V**	**Step I**	**Step II**	**Step III**	**Step IV**	**Step V**
No Etch	106	102			115	341	246			174
Etched	-	-	144	71	64	-	-	150	67	69

* Particle swipe value of less than level 83 is acceptable.

Figure 3 shows the surface morphology of the sample with machined surface at three magnifications of 100X, 500X and 2,000X. This sample did not receive the phosphoric acid etching. At high magnification, the machined surface was severely torn with fish-scale like pattern. Even after the rigorous gross and precision cleanings with high pressure spray of Brulin detergent, it is evident that many sub-micron aluminum particles (as indicated by arrows) were still adhered to the rough surface. This resulted in high particle swipe value of level 115.

Figure 4 shows the surface morphology of a sample with a machined surface that had been etched with 30% phosphoric acid for 30 minutes prior to cleaning. The machine-torn surfaces were smoothed out slightly by the H_3PO_4 etching and the sub-micron aluminum particles were no longer present on the surface. However, the H_3PO_4 also attacked the Mg_2Si precipitates in the matrix and left many pits (as indicated by arrows) behind. The particle swipe values increased right after the acid etch in both types of sample. However, after the precision cleaning, the surface was much cleaner and the swipe values decreased significantly.

As shown in **Figures 5** and **6**, the samples with mill-finished surfaces exhibited similar results as that of the samples with machined surfaces. In **Figure 5** and **Table II**, the mill-finished surface appeared to have many more aluminum particles than that of the machined surface. These fine particles are typical of the aluminum fines generated by the rolling process in the aluminum mill. After the phosphoric acid etch and precision cleaning, the mill-finished surface also reached an acceptable level.

DISCUSSIONS

Over the past year, there are several observations often encountered during the cleaning of various aluminum alloys. In general, these observations can be summarized as follows:

1. After several rigorous (high pressure spray) washes with alkaline detergent (Brulin® with pH ~ 10), most of the particles larger than one micron could be washed away. However, many sub-micron aluminum particles were still firmly attached to the aluminum surfaces as revealed by smudges on the swipe papers.

2. Other types of sub-micron particles that are alien to aluminum alloys, such as iron oxide and stainless steel, were also found on the aluminum surfaces after cleaning.

3. After the gross/precision cleaning, the "smut" sometimes re-appears several days later.

4. During the drying of precision washed parts, high hot air temperature could cause the smut to appear. The OAB has since reduced the hot air temperature from 225°F to 150°F to prevent this phenomenon from occurring.

5. Hand-wiping the aluminum surface with polar solvent after the detergent wash helped to remove these sub-micron particles. This is one of the key remedial cleaning steps in bringing down the particle swipe value to below level 83.

6. Etching the aluminum surfaces with phosphoric acid (30 vol% / 30 min.) before the detergent wash helps to remove the sub-micron particles during the detergent wash.

Apparently, to explain the observations listed above , we require a fundamental understanding about the affinity of sub-micron metallic particles attracting to the aluminum surface. A mechanism, based on the ζ-potential, is proposed as follows:

<u>Electric Double Layer</u> It is well known that the surfaces of all aluminum alloys are actually covered by a thin layer of aluminum oxide (Al_2O_3). When this oxide film is exposed to water, depending on the temperature and time of the exposure, it will form various forms of hydroxides, such as bayerite, gibbsite and nordstrrandite $Al(OH)_3$, boehmite and diaspore (AlOOH), and γ-Al_2O_3 and corundum[3]. However, all the hydroxides have a hydroxyl lattice structure in which the bound oxygen atoms will orient the adjacent water molecules to balance the dipole charges over a small distance often called "the electric double layer"[4]. As the particle size becomes smaller than 1 micron, the influence of the electrostatic potential in this double layer becomes more dominant in affecting the electrochemical behavior of these fine particles.

An electrostatic attractive force[5], the ζ-potential, can be established between the aluminum surface and the sub-micron particle by the negatively charged hydroxide, oriented water molecules and the abundant supply of cations in the detergent water as illustrated in **Figure 7**. This electrostatic force is likely the reason that many sub-micron particles are still able to adhere to the aluminum surfaces after the detergent wash. The hydrated aluminum surface not only attracts the aluminum particles, but also all metal oxide particles, such as iron, stainless steel, etc. The existence of a ζ-potential on aluminum surface helps to explain the **Observations 1 & 2.**

After the detergent wash, the aluminum surfaces are exposed to ambient air. However, water molecules are still trapped between the particle and the aluminum surface and maintain the strong electrostatic attraction. Over time, the aluminum hydroxides do dehydrate to various forms of Al_2O_3 in air or in inert atmosphere[3]. The dehydration, either through the exposure to ambient air, forced hot air or solvents, takes away the binding agent, water molecules, between the sub-micro particles and the aluminum surface. Thus, the electrostatic attractive force weakens over time and renders the sub-micron particles easy to remove through a physical wiping. The dehydration process helps to explain the **Observations 3, 4 & 5.**

It has been established that the etching of aluminum surfaces with phosphoric acid before detergent wash helps to remove the small sub-micron particles during cleaning. Although this has become a routine process for cleaning of NIF parts, the reason that it is effective isn't clearly understood. There are three possible mechanisms involved in the acid etching process:

a. **Dissolving the aluminum particle** **Figure 8** shows the SEM micrographs of an aluminum surface before, versus after, the phosphoric acid etching. Before the phosphoric acid etching, there are many sub-micro particles attached to the surface. Most of these particles disappeared after the phosphoric acid etch and the aluminum surface was also etched slightly by the acid. Thus, the phosphoric acid indeed removed the fine particles by dissolving them. Experimental results show that the particles swipe value often increased right after the phosphoric acid etch as shown in **Table II** and in **Reference 2.** This suggests that more debris were generated during the etching process. However, these debris could be easily washed away by the subsequent cleaning process. Thus, the phosphoric acid not only dissolved the aluminum particles, but also in some way changed the nature of the aluminum surface.

b. **Changing the nature of the surface** It is possible that the phosphoric acid can react with $Al(OH)_3$ to form $AlPO_4$ as

$$Al(OH)_3 + H_3PO_4 \rightarrow 3H_2O + AlPO_4\ ,$$

thus changing the nature of the aluminum surface. A sample etched with 30% phosphoric acid for 30 minutes had been analyzed by the XPS. Although a small P peak (~ 133.8 eV) was detected on the surface as shown in **Figure 9**, a careful analysis of the binding energies of P, O and Al offered no conclusive evidence that $AlPO_4$ was formed. Instead, the XPS data suggests the formation of a metaphosphate, $Al(PO_3)_3$, on the aluminum surface.

c. **Changing the ζ-potential of the aluminum surface** It is also known[4] that the magnitude of the ζ-potential can be altered by adjusting the pH in the aqueous solution. As the pH is lowered by the phosphoric acid, the ζ-potential of the $Al(OH)_3$ is either reversed or approaches zero. This reduces the attraction force and makes it easier to remove the sub-micron aluminum particles. Future experiment will be conducted to measure this effect.

CONCLUSIONS

- The smut that appeared on the universal covers after the OAB cleaning process was sub-micron size aluminum particles originated from the machining or mill rolling processes.
- The rigorous gross and precision cleanings with Brulin could not completely dislodge these fine particles from the surface. However, a phosphoric acid etch before the cleaning helped to remove these fine aluminum particles.
- An acid etching before cleaning is essential in preventing the occurrence of smut in aluminum alloy after gross/precision cleaning.
- A mechanism, based on the electrostatic ζ-potential, is proposed to explain the occurrence of smut that is often encountered during the cleaning of aluminum alloys

ACKNOWLEDGEMENTS

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The valuable discussions with Nerine Cherepy on surface electrochemistry help the author to propose the ζ-potential mechanism. As always, the encouragements and suggestions offered by Bill Gourdin during the course of this investigation and the reviewing of this manuscript are also greatly appreciated.

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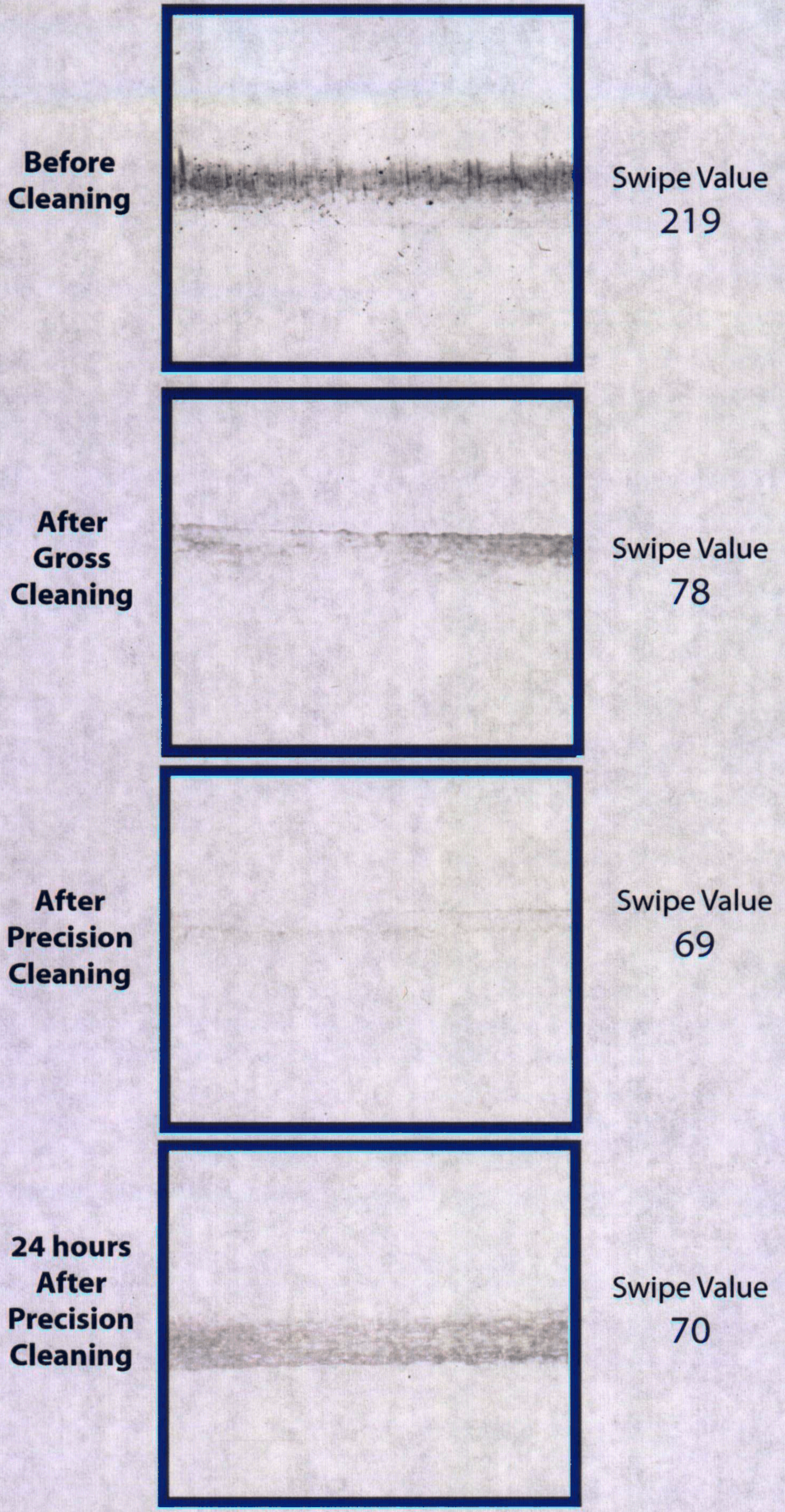


Figure 1 After the OAB cleaning, the particle swipe reached an acceptable level of below level 83. However, the smuts were still visible from the swipe paper. The smut problem appeared to be worsen 24 hours after the precision cleaning.

Figure 2 The SEM-BSE image of the particles on the swipe filter paper collected from the universal cover after the gross cleaning in OAB. This universal cover did not receive the phosphoric acid etch before cleaning.

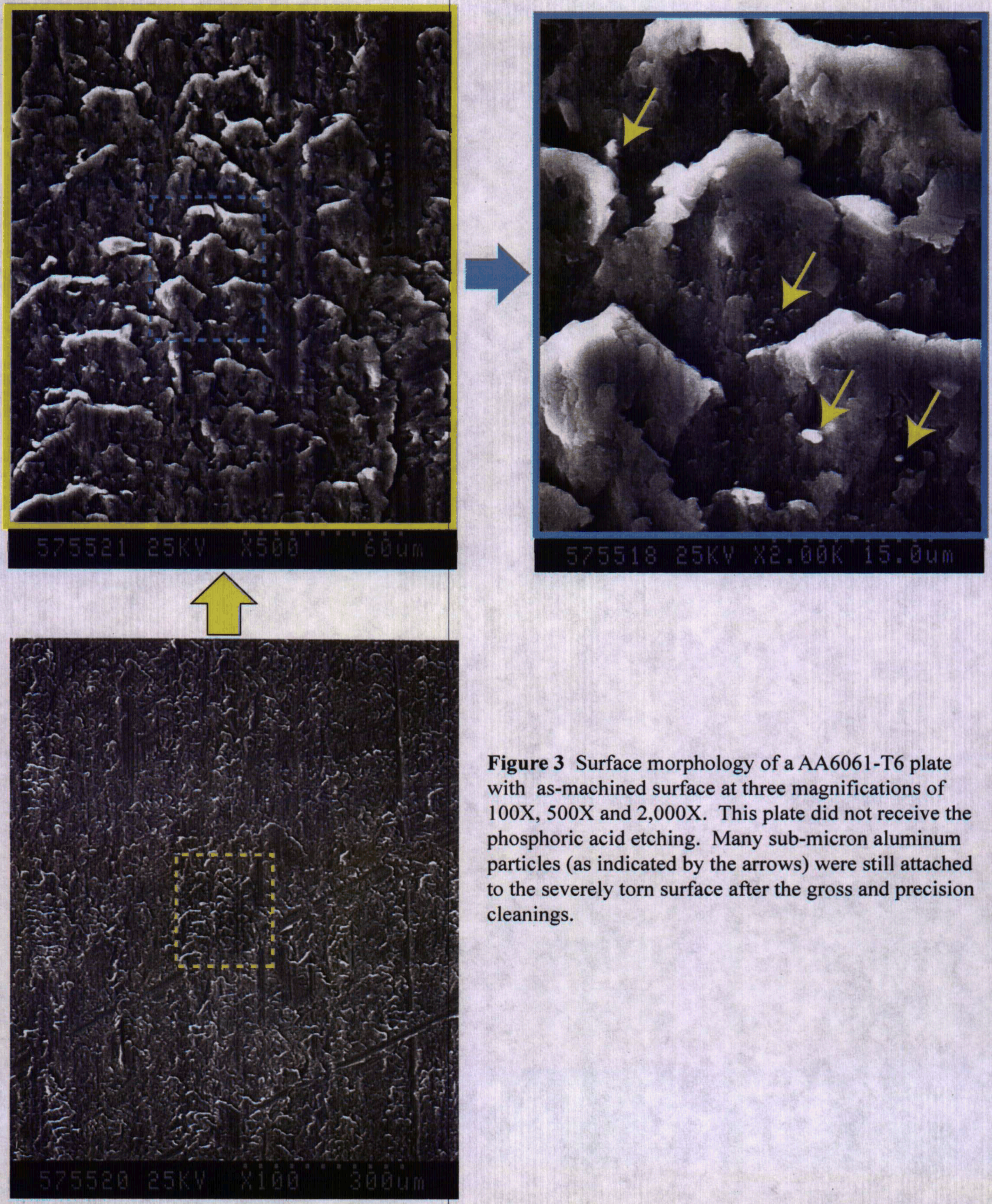


Figure 3 Surface morphology of a AA6061-T6 plate with as-machined surface at three magnifications of 100X, 500X and 2,000X. This plate did not receive the phosphoric acid etching. Many sub-micron aluminum particles (as indicated by the arrows) were still attached to the severely torn surface after the gross and precision cleanings.

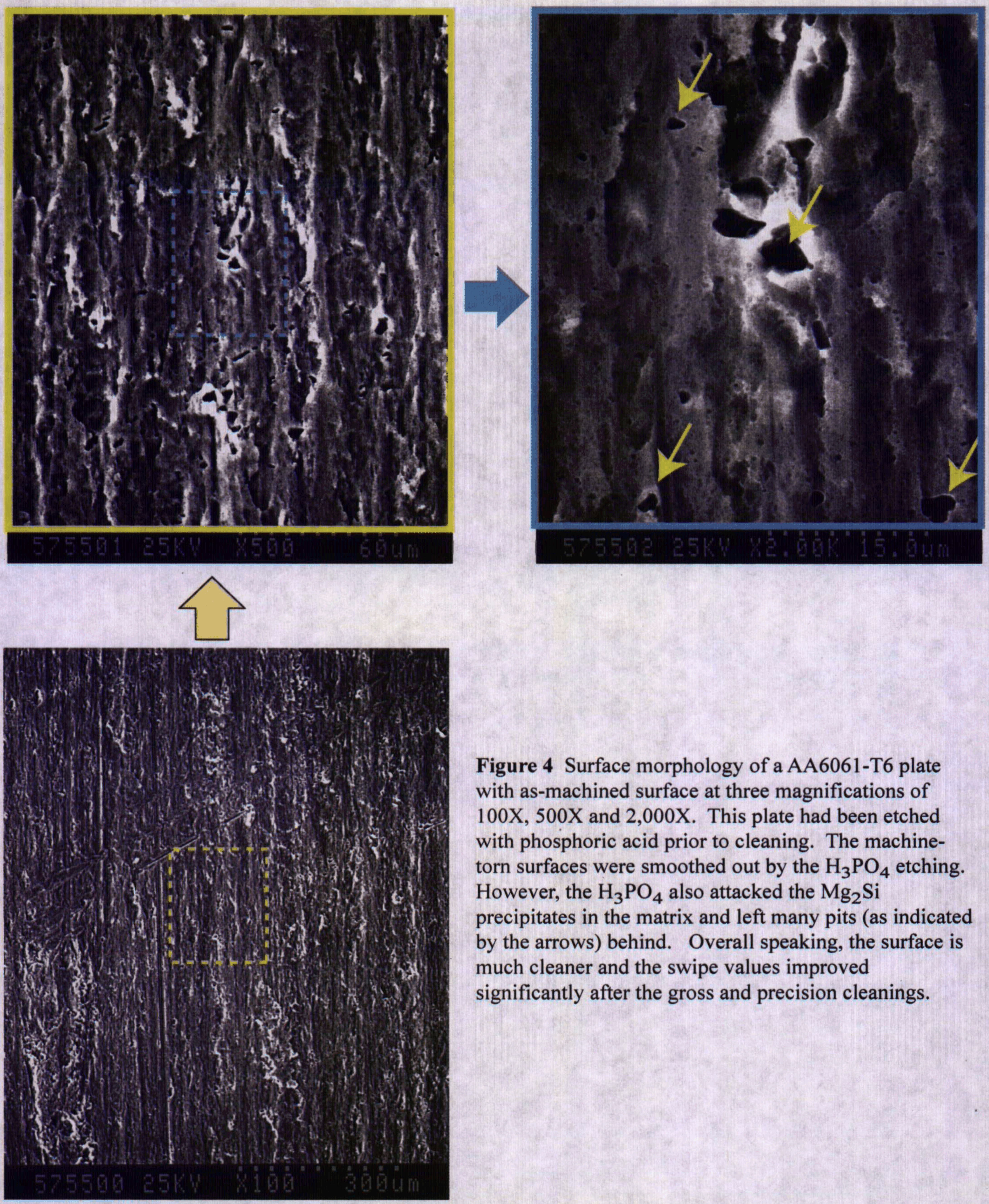


Figure 4 Surface morphology of a AA6061-T6 plate with as-machined surface at three magnifications of 100X, 500X and 2,000X. This plate had been etched with phosphoric acid prior to cleaning. The machine-torn surfaces were smoothed out by the H_3PO_4 etching. However, the H_3PO_4 also attacked the Mg_2Si precipitates in the matrix and left many pits (as indicated by the arrows) behind. Overall speaking, the surface is much cleaner and the swipe values improved significantly after the gross and precision cleanings.

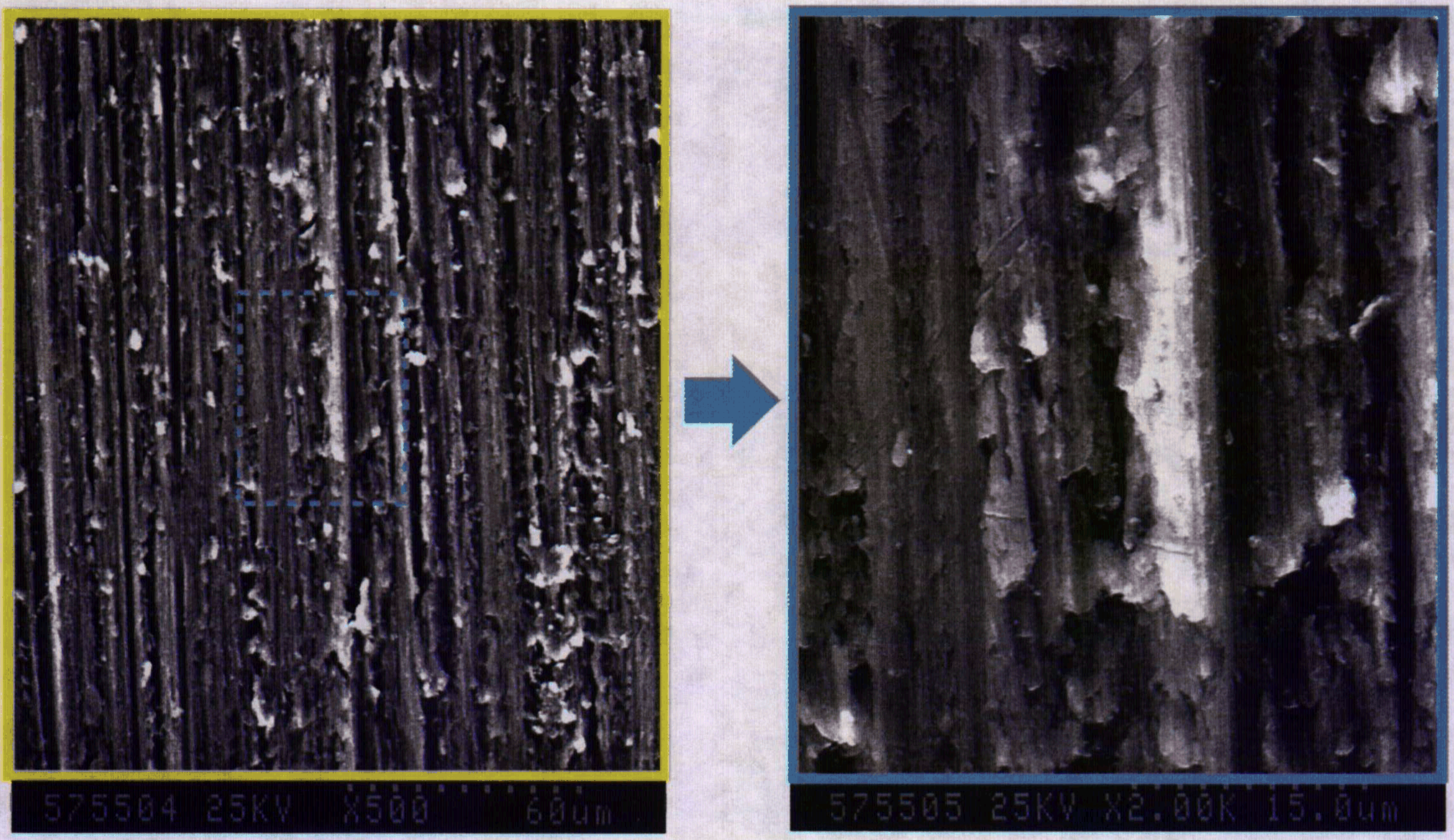


Figure 5 Surface morphology of a AA6061-T6 plate with mill-finishedsurface at three magnifications of 100X, 500X and 2,000X. This plate did not receive the phosphoric acid etching. Many sub-micron aluminum particles were still attached to surface after the gross and precision cleanings.

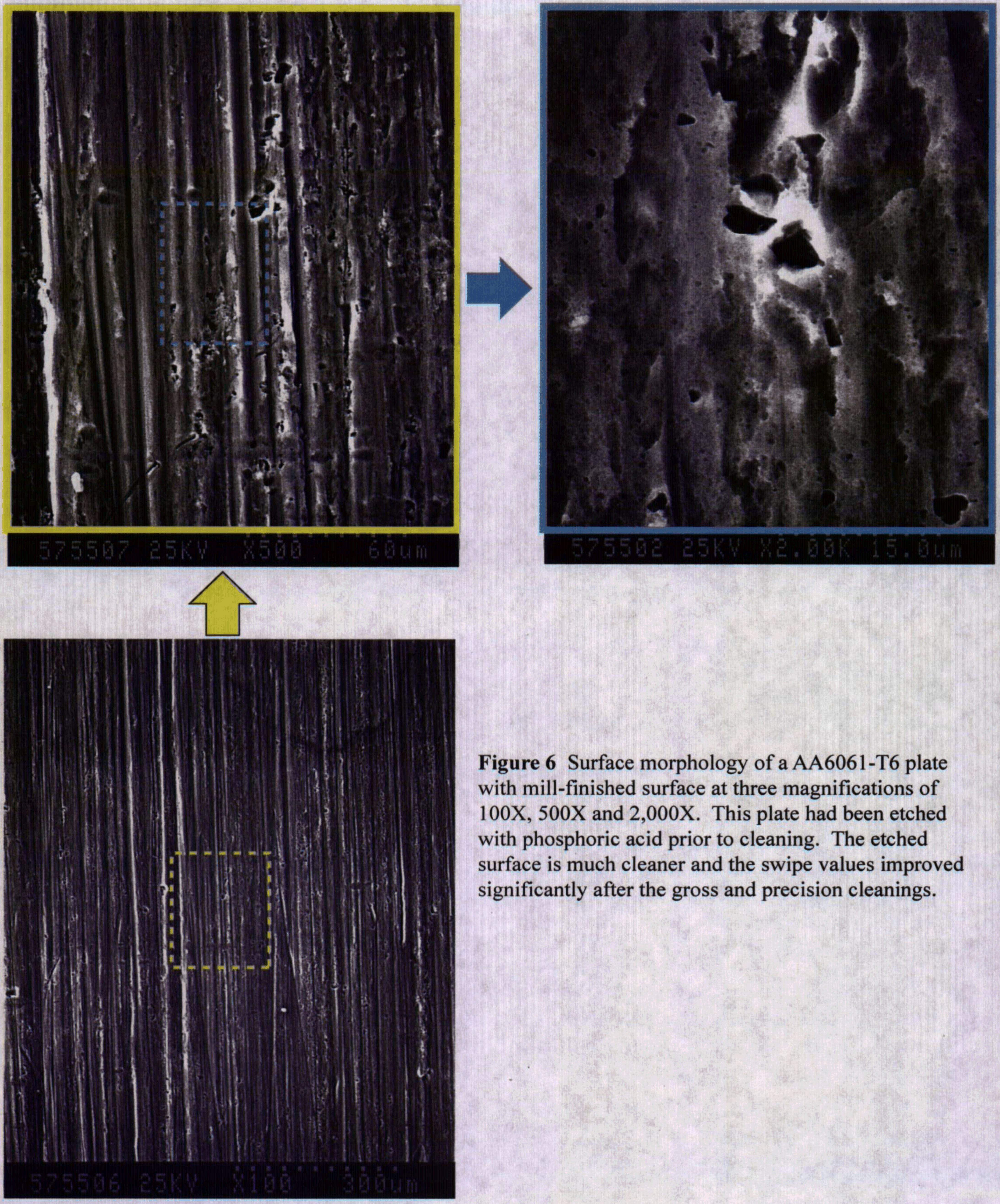


Figure 6 Surface morphology of a AA6061-T6 plate with mill-finished surface at three magnifications of 100X, 500X and 2,000X. This plate had been etched with phosphoric acid prior to cleaning. The etched surface is much cleaner and the swipe values improved significantly after the gross and precision cleanings.

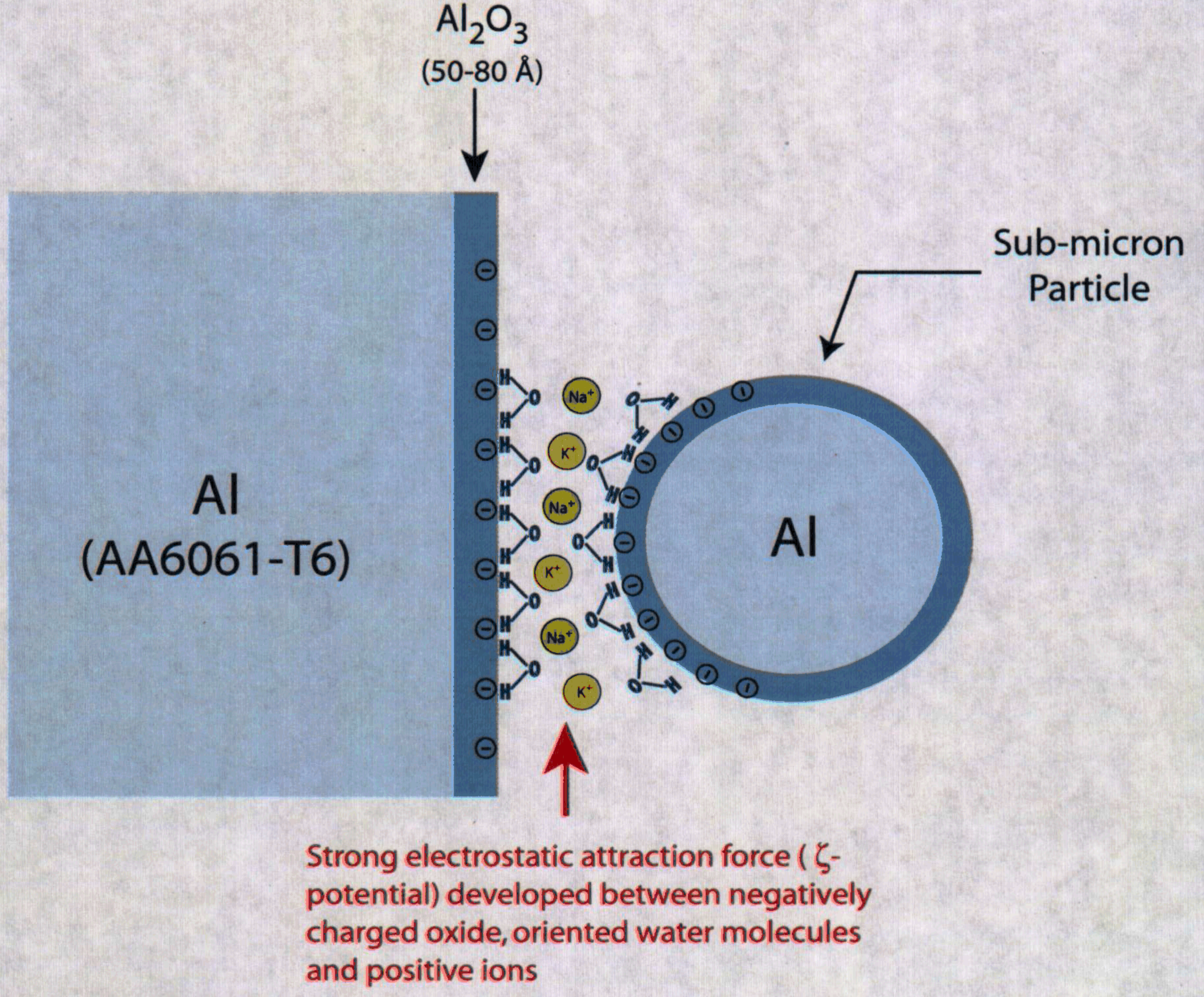


Figure 7 A proposed mechanism to explain how the sub-micron particles adhere to the aluminum surfaces.

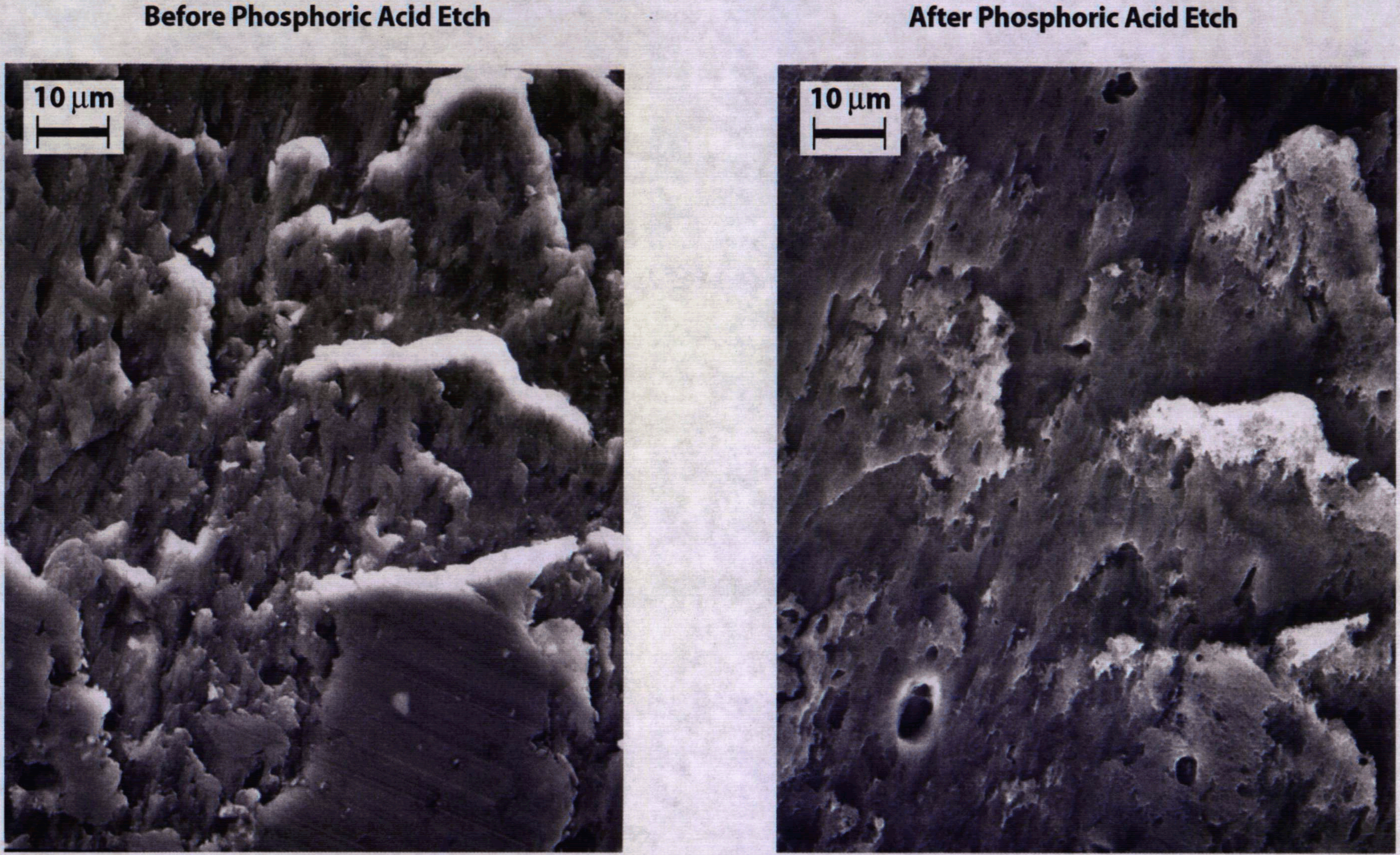


Figure 8 The phosphoric acid dissolved the sub-micron aluminum particles and etched slightly the aluminum surfaces.

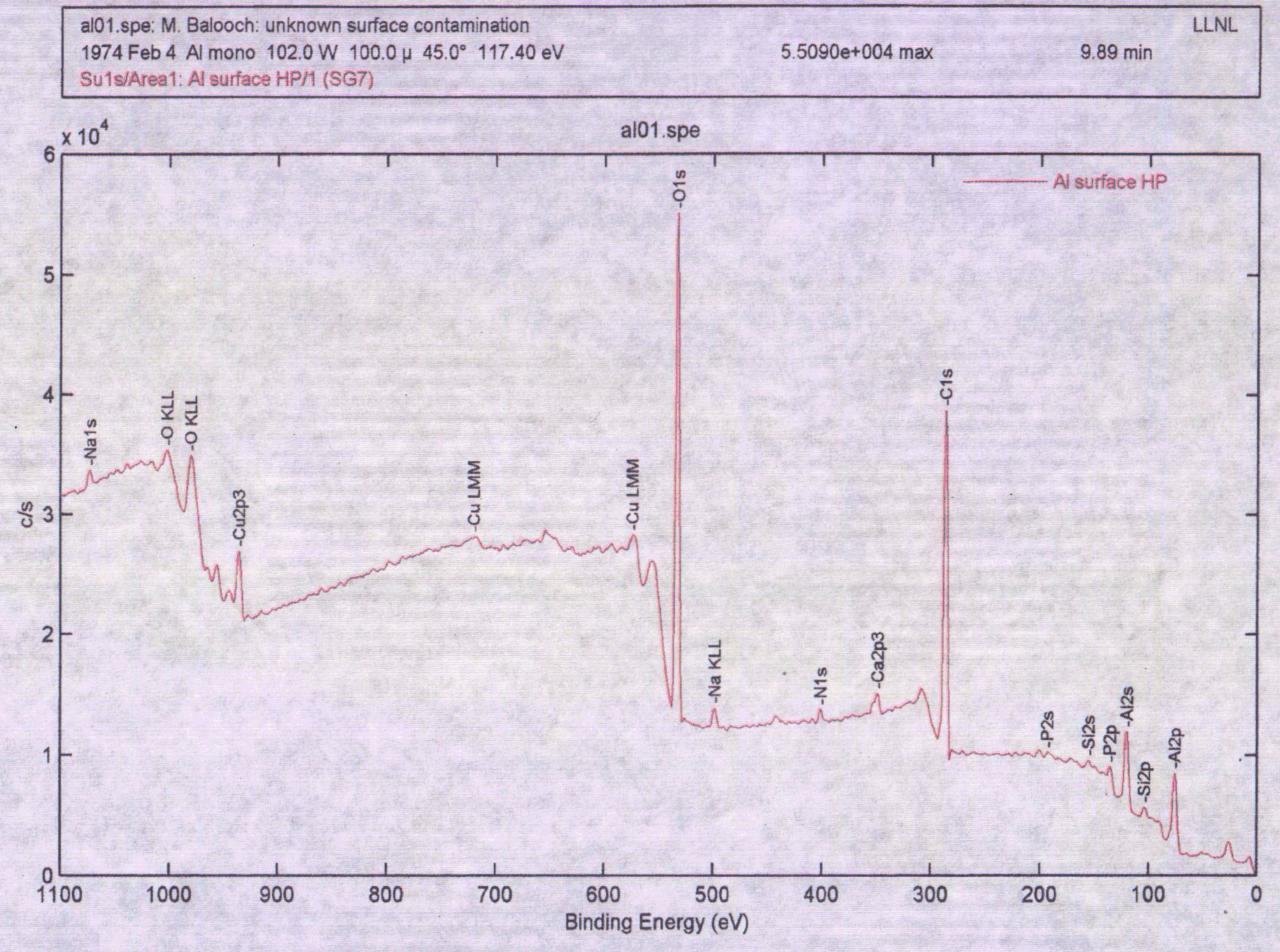


Figure 9 The XPS result on a aluminum sample etched with 30% phosphoric acid. Small P peak was detected at 133.8 eV.

Appendix I

OAB Cleaning Process Procedure for Aluminum

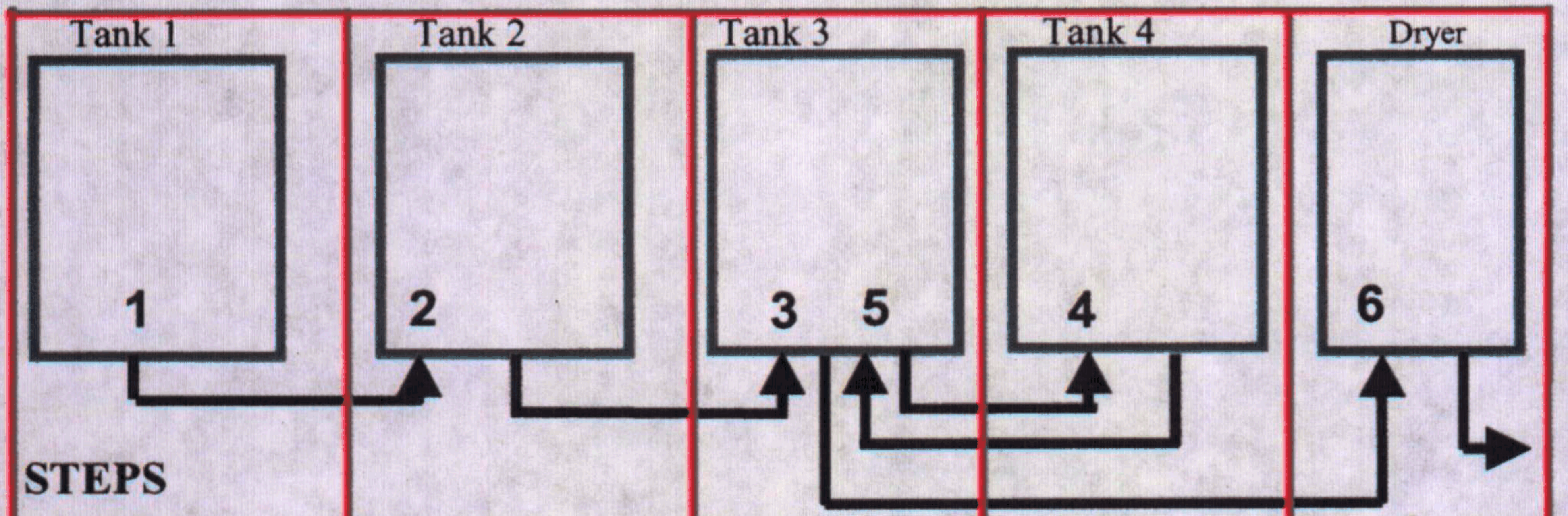
Gross Cleaning Process (Aluminum) Formula G1 12/7/2000

Parameters:	Pressure	2500 PSI
	Surfactant	3-5% Brulin 1990GD
	Rinse	10-18 Mega-ohm DI Water
	Angle	~ 45 degrees
	Direction	Top to bottom & side to side
	Temperature	130-150^0 F

Process:

1. High Pressure spray one side of the part with Brulin at 8 - 10" away from the surface at a rate of aproximately 6"/sec. Spray top to bottom and side to side.
2. Use a coarse brush to scrub the surface one time with a circular motion and side to side on the edges.
3. Repeat the Brulin spray as in step 1.
4. Use a medium brush to scrub the surface one time with a circular motion and side to side on the edges.
5. Flip the part to clean the other side.
6. Repeat steps 1 - 4 on the second side.
7. High Pressure spray both sides of the part with Brulin at 1-3" away from the surface at a rate of 3-4"/sec.
8. High Pressure DI Spray 1-3" from the part at a rate of 3-4"/sec. Spray top to bottom and side to side.
9. Transport to Class 1000 Precsion Mechanical cleaning Room
10. Precision clean parts utilizing the Small Mechanical Parts Gross and Precision Cleaner

Precision Cleaning Process: Automated Ultrasonic Cleaner (for Small Parts)

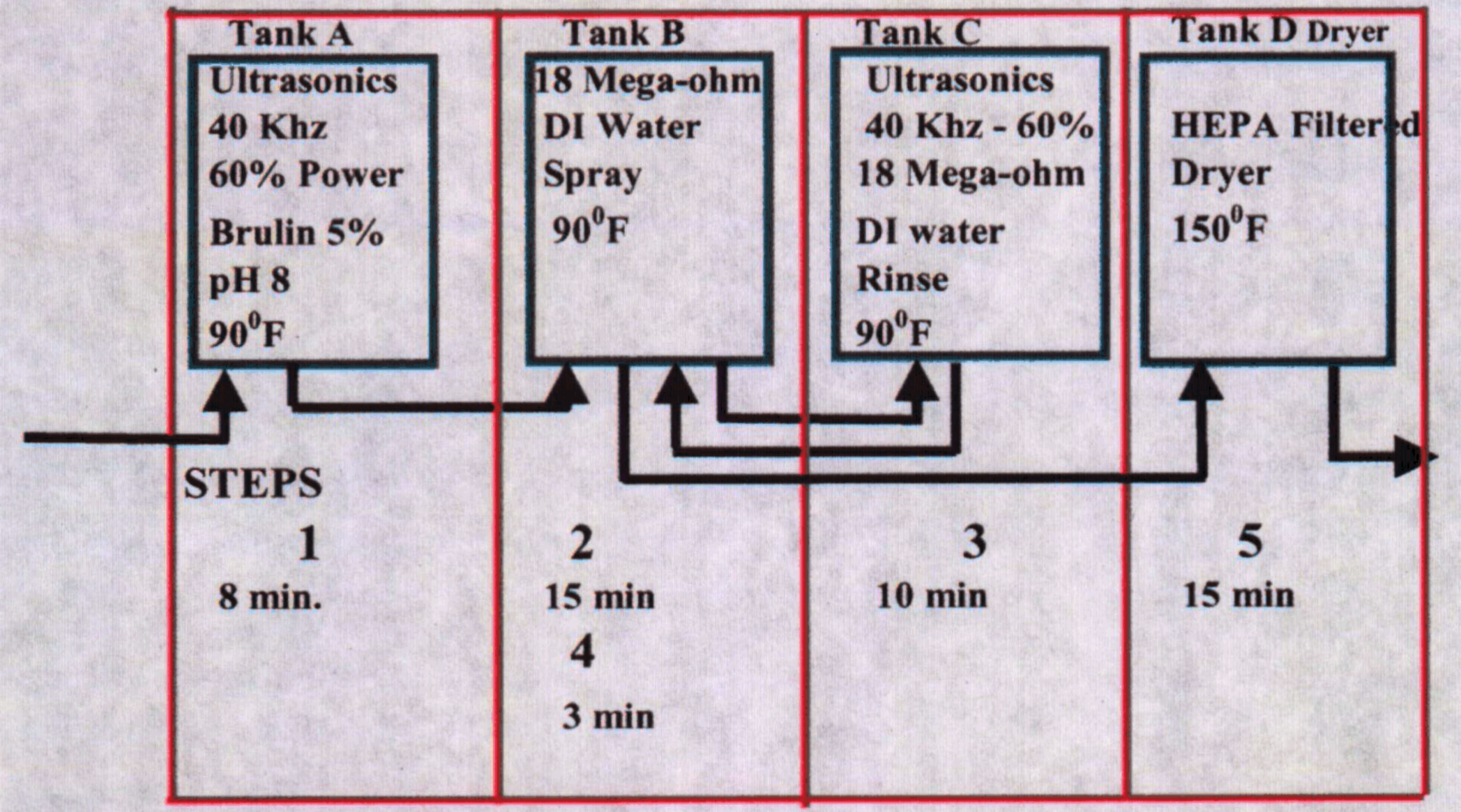


STEPS

1 Prewash HP Spray 5% Brulin 1990GD 145^0 F **10 Min.**	**2** 60% Power U.S. 10% Brulin 815GD **30 min.** 150^0 F	**3** HP Low Flow DI - **15 min.** **5** LP High Flow DI - **15 min.**	**4** 60% power U.S. DI **15 min.**	**6** 1500 **15 min.** 150^0 F

Version 1.1
3/27/2001

OAB Large Mechanical Parts Precision Cleaner



Version 1

Appendix II

Results of EDS analysis on the particles in swipe paper

st: strong peak; m: medium; t: trace

Before Cleaning

	Size (µm)	O	N	Mg	Al	Si	S	Cl	Ca	Ti	Cr	Fe	Ni	Cu	Type of Particle
P9	15 x 15											st			Iron
P12	10 x 5				st										*Al* particle
P1	10 x 10	m			st	m			m			t			Al + lubricant
P7	10 x 10				st										*Al* particle
P2	5 x 5	st	m		st	t		m	m						Al + lubricant
P10	5 x 5	st		m	m	st	t		st						Al + lubricant
P8	5 x 3	m			st		m		m						Al + lubricant
P3	3 x 1	t			st										*Al* particle
P6	2 x 2				st										*Al* particle
P4	2 x 0.5				st										*Al* particle
P11	2 x 0.5				st										*Al* particle
P5	1.5 x 0.2				st										*Al* particle

After Gross Cleaning

	Size (µm)	O	N	Mg	Al	Si	S	Cl	Ca	Ti	Cr	Fe	Ni	Cu	Type of Particle
P11	4 x 0.5				t	t					st	st	m		stainless steel
P6	2 x 2				st										*Al* particle
P7	2 x 2				m							st			-
P12	2 x 2				st										*Al* particle
P5	2 x 0.5				st										*Al* particle
P8	2 x 0.5				t	t					st	st	m		stainless steel
P1	1.5 x 1	t			st										*Al* particle
P19	1.5 x 1				st										*Al* particle
P3	1 x 1	t			m							st			Iron oxide
P10	1 x 1	t			m							st			Iron oxide
P13	1 x 1				st										*Al* particle
P14	1 x 1				t							st			Iron oxide
P15	1 x 1				st										*Al* particle
P17	1 x 1				st										*Al* particle
P9	1 x 0.5				st										*Al* particle
P16	1 x 0.5				st										*Al* particle
P18	1 x 0.5											st			Iron oxide
P2	0.5 x 0.5				st										*Al* particle
P20	0.5 x 0.5				st										*Al* particle
P4	0.5 x 0.3	t			st										*Al* particle

After Precision Cleaning

	Size (µm)	O	N	Mg	Al	Si	S	Cl	Ca	Ti	Cr	Fe	Ni	Cu	Type of Particle
P1	10 x 1				st										*Al* particle
P15	7 x 3				st										*Al* particle
P11	3 x 1				st										*Al* particle
P8	2 x 3				st	t						t			α-eutectic
P7	2 x 1				st										*Al* particle
P13	2 x 0.5				st										*Al* particle
P20	2 x 0.5				st										*Al* particle
P17	1 x.5				st										*Al* particle
P4	1 x 1				st										*Al* particle
P5	1 x 1										st	st	st		stainless steel
P6	1 x 1				st										*Al* particle
P9	1 x 1				st	t						t			α-eutectic
P10	1 x 1				st										*Al* particle
P12	1 x 1			t	st	t									*Al* particle
P16	1 x 1	st										st			Iron oxide

P19	1 x 1				st										*Al* particle
P2	0.5 x 0.5											st			Iron oxide
P3	0.5 x 0.5										st	st	st		stainless steel
P18	0.5 x 0.5	st			t							st			Iron oxide
P14	0. 5x 0.5				st	t						t			α-eutectic

24 Hours After Precision Cleaning

	Size (µm)	O	N	Mg	Al	Si	S	Cl	Ca	Ti	Cr	Fe	Ni	Cu	Type of Particle
P8	5 x 2			t	st	t									*Al* particle
P2	4 x 2				st	t						t			α-eutectic
P5	4 x 2	m		t	st	t									*Al* particle
P16	3 X 2				st	t									*Al* particle
P3	3 x 1	m			st	t						t			α-eutectic
P15	3 x 1				st	t									*Al* particle
P11	3 x 0.5			t	st	t									*Al* particle
P6	2 x 2	m			m	t		m	m		t	m			stainless steel
P20	2 x 1				st										*Al* particle
P4	2 x 0.5	m		t	st	t									*Al* particle
P7	2 x 0.5	t			st	t						t			*Al* particle
P13	10 x 3	st			t					st					TiO_2
P1	10 x 10	m	st		m		m	m			st				detergent
P9	1.5 x 1.5	m			m										*Alumina*
P14	1.5 x 1.5				t						st	st	t	t	stainless steel
P10	1 x 1	st			t						st	st			stainless steel
P17	1 x 0.5				st	t									*Al* particle
P18	1 x 0.5				st	t									*Al* particle
P19	1 x 0.5				st	t						t			*Al* particle
P12	0.5 x 0.5	m			st										*Al* particle